



Electrochemical performance of spin coated dense $\text{BaZr}_{0.80}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ membranes

Igor Luisetto^{a,b,c}, Silvia Licoccia^{a,b}, Alessandra D'Epifanio^{a,b}, Alessandra Sanson^d, Elisa Mercadelli^d, Elisabetta Di Bartolomeo^{a,b,*}

^a Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

^b NAST Centre, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

^c Department of Mechanical and Industrial Engineering, University of Rome Tre, Via Vasca Navale 79, 00146 Rome, Italy

^d CNR-ISTEC, Institute of Science and Technology for Ceramics, National Research Council, Via Granarolo 64, Faenza, Italy

H I G H L I G H T S

- Synthesis of $\text{BaZr}_{0.80}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ by citric acid-nitrate auto-combustion method.
- Reproducible spin coated dense electrolyte.
- Optimized anodic support.
- Improved power output at 600 °C.
- Higher performance in comparison with literature data.

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The high sintering temperature of Yttrium doped barium zirconate (BZY), the most promising high temperature proton conductor (HTPC) for Intermediate Temperature (400–750 °C) Solid Oxide Fuel Cells (IT-SOFCs), has been reduced by using ZnO as a sintering aid. Obtaining a dense electrolyte at a reduced temperature allows conventional fuel cell preparation methods.

A reproducible spin coating method to fabricate highly performing anode supported button cells with dense micrometric BZY_{Zn} electrolyte layers has been developed. The electrochemical characterization of button cells at 600 °C shows promising performance, higher than that of comparable fuel cells from literature.

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1. Introduction

High temperature proton conductors (HTPCs) have been widely investigated as potential electrolytes materials for Intermediate Temperature (400–750 °C) Solid Oxide Fuel Cells (IT-SOFCs) [1–4]. Yttrium doped barium zirconate (BZY) has emerged as appealing electrolyte because of its high conductivity and good chemical stability [5–7]. Its highly refractory nature has driven investigations on the development of proper processing protocols aiming to

achieve high-density and large grained material at reasonable sintering temperatures, thus reducing costs and improving the overall conductivity [8,9]. Different methods, such as the preparation of BCY-BZY solid solutions [10–12], the synthesis of ultrafine powders [13–15], the use of sintering aid [16–20] have been exploited to achieve this aim. The reduction of the sintering temperature allows the fabrication of co-sintered fuel cells assuring enough electrode porosity and reducing chemical reactions at the electrode–electrolytes interface.

The use of ZnO has been extensively investigated and densities larger than 90% have been obtained at temperatures of about 1300–1450 °C, associated with a slight decrease of proton conductivity [16,21–24]. The considerably lower sintering temperature, compared to the undoped BZY, make $\text{BaZr}_{0.80}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ (BZY_{Zn}) a promising electrolyte for the

* Corresponding author. Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy. Tel.: +39 06 7259 4495; fax: +39 06 7259 4328.

E-mail address: dibartolomeo@uniroma2.it (E. Di Bartolomeo).

preparation of dense electrolyte membrane on porous anode with conventional fuel cell preparation methods.

Several preparation methods have been exploited for the preparation of thin and thick proton conducting membrane such as tape casting [25], electrophoretic deposition (EPD) [26,27], pulsed laser deposition (PLD) [28], co-pressing [29,30], spray coating [31], and slurry spin coating [32]. Among them, slurry spin coating is a simple and cost effective method that allows the control of the electrolytes thickness by varying the coating cycles. It can be used for the deposition of electrolytes membrane over a pre-sintered porous cermet thus overcoming some limits of other preparation methods mentioned above, such as delamination and cracks occurring during the co-sintering step in the co-pressing and tape-casting methods, the requirement of conducting substrates for EPD, and the need of flat and pores free substrates for PLD.

Aim of this work is to set up a reproducible spin coating method to fabricate at lab-scale highly performing anode supported button cells with dense micrometric BZYZn electrolyte layers, and to investigate the electrochemical performances and comparing them with results from literature.

2. Experimental

$\text{BaZr}_{0.80}\text{Y}_{0.16}\text{Zn}_{0.04}\text{O}_{3-\delta}$ (BZYZn) perovskites powders were prepared by a citric acid-nitrate auto-combustion method as previously described [33,34].

Green cermet anodes were prepared by die pressing method: NiO nanometric powders (Sigma Aldrich) and BZY in a weight proportion 60:40 were planetary milled in ethanol solvent with BUTVAR 98 (5 wt %) (Sigma Aldrich) as binder for 4 h. Next, micrometric graphite (10 wt %) (Sigma Aldrich) was added as pore forming agent and milled for another hour. The slurry was dried over the night at 75 °C and grounded in an agate mortar for 4 or 8 h. The powder was uniaxially pressed into cylindrical pellets with a 13 mm stainless steel die at 250 MPa and pre-sintered at 1000 °C for 3 h with a ramp of 5 °C min⁻¹ with an intermediate step at 600 °C for 2 h to burn out all the organics.

Structural and morphological characterizations of powders and pellets were performed by X-ray diffraction (XRD) analysis (Philips X-Pert Pro 500 Diffractometer) and field emission scanning electron microscopy (FE-SEM, Leo Supra 35).

To investigate the shrinkage mismatch between the anode substrate and the electrolyte layer to be deposited, dilatometric measurements were carried out in airflow (100 mL min⁻¹) on the corresponding powders uniaxially pressed in bars (340 MPa). The analyses were performed between 20 and 1500 °C at 5 °C min⁻¹ heating rate by a Netzsch dilatometer 402E, Germany.

Dense BZYZn membranes were fabricated by spin coating technique. BZYZn (25 wt %) was planetary milled in organics solvent (terpineol:ethanol 1:1 vol %) with BUTVAR 98 as binder (5 wt %) and PEG400 (3 wt %) and DBP (3 wt %) as plasticizers to form a stable colloidal slurry. The stable BZYZn containing colloidal slurry was obtained milling the components for different times from 1 to 10 h at 350 rounds min⁻¹ (higher rates were avoided to prevent overheating of the slurry).

The green pre-sintered cermet was vacuum fixed on the chuck of the coater (Laurell model WS-400-6NPP) and the electrolyte slurry was spin coated at a rotating speed of 6 krpm for 30 s. The coated substrate was dried at 120 °C for 30 min and thermally treated at 400 °C for 1 h to remove the organics. The spin coating process was repeated until the desired electrolyte thickness was obtained. The half cell was co-sintered at 1450 °C for 5 h.

To form a complete single button cell, Pt paste was paint brushed on the electrolyte surface and fired at 850 °C for 30 min. Gold wires were fixed with a drop of Pt paste on the top of the

anode and cathode and used as current collectors. For fuel cell tests, the samples were mounted at the end of an alumina tube using a gas tight ceramic paste seal (Aremco, 552). The cathode was exposed to static air while the anode to wet H₂ (~3% H₂O). Hydrogen-air fuel cell experiments were carried out at 600 °C. Electrochemical tests were performed using a potentiostat/galvanostat/FRA PARSTAT 2273. Structural and morphological characterization of fuel cells were performed both before and after the single cell test.

3. Results and discussion

Fig. 1 shows the sintering behaviors of BZY, BZYZn, and NiO-BZY green cermet anode. BZYZn started shrinking at 1100 °C reaching a maximum of 21% at 1460 °C, almost 4 times the maximum shrinkage of undoped BZY which is about 5.5%. At temperatures higher than 1460 °C, BZYZn tends to expand, indicating a reduction of density that, on the basis of literature data [16], can be ascribed to Zn evaporation. NiO-BZY showed a gradual shrinkage below 700 °C due to the burn out of the pore forming additive; the onset of sintering was at 1000 °C and a maximum shrinkage of 26% was reached at 1450 °C. Thus, 1000 °C was chosen as the pre-sintering temperature of NiO-BZY anode to provide it with enough mechanical strength to be used as substrate and to have, at higher temperatures, a comparable shrinkage behavior to BZYZn film to be spun onto its surface.

Fig. 2 shows the SEM micrographs of sintered anodic substrates grounded for 4 and 8 h, respectively. By using a longer grinding time it is possible to obtain a more uniform morphology with well dispersed micrometric NiO grains (darker particles) without any agglomeration allowing a better percolation path for the electronic conduction. A micrometric porosity is preserved in both cases.

Fig. 3(a) and (b) show the SEM micrographs of 20 µm thick films after co-sintering at 1450 °C, obtained milling the BZYZn containing colloidal slurry for 1 h and 10 h, respectively. Fig. 3(a) clearly shows the presence of micrometric aggregates, while Fig. 3(b) shows a fully densified electrolyte with random distributed grains of micrometric and sub-micrometric sizes, without penetrating cracks or pinholes. Thus, a long milling time, at least 10 h, is necessary to remove micrometric aggregates in the deposited layers. For shorter milling times, porous and inhomogeneous layers were obtained.

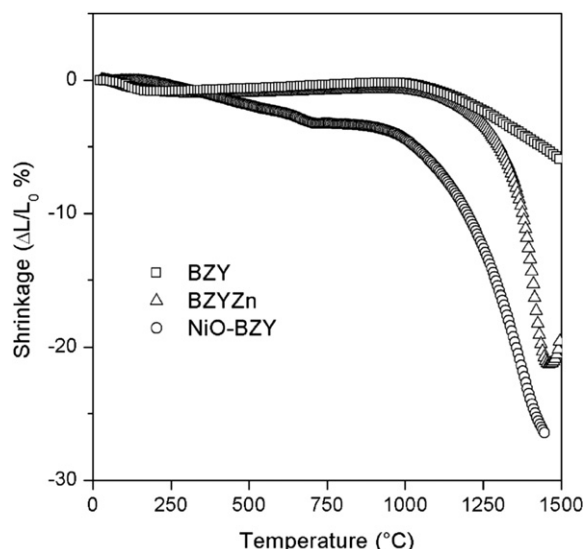


Fig. 1. Shrinkage curves of BZY, BZYZn green electrolytes and NiO-BZY green cermet.

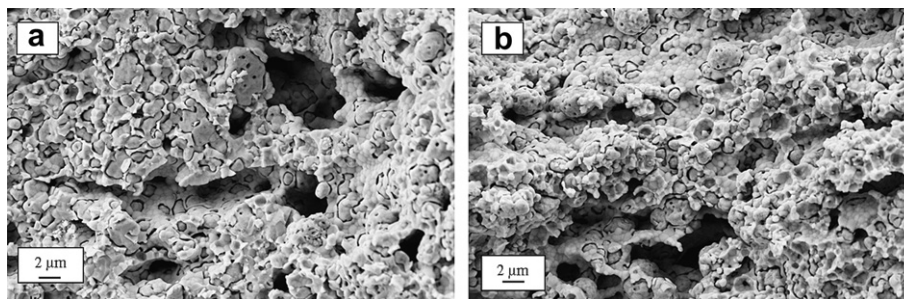


Fig. 2. SEM micrographs of sintered anodic substrates grounded for: (a) 4 and (b) 8 h.

BZYZn films of different thickness were deposited by increasing the number of spun layers. After the deposition of each layer, the sample was dried at 120 °C and thermally treated at 400 °C to remove the organics and avoid the formations of pinholes. Increasing the number of deposited layers from 3, 4 to 6, the BZYZn films thickness increased from 10, 15–20 μm, respectively. Fig. 4(a) and (b) show the SEM micrographs of the surface fracture of 3 layers and 6 layers BZYZn deposited films on the anodic substrate. The electrolytes showed thicknesses of about 10 μm (Fig. 4(a)) and 20 μm (Fig. 4(b)) and good adhesion to the anodic support, revealing microstructures free of cracks and fully densified except for some close porosities. A transgranular fracture is clearly detectable in the electrolyte especially in Fig. 4(a) where a larger magnification was used. The anodic supports showed an appropriate macroporosity.

Layers of 20 μm thickness were chosen for fuel cells tests because they ensure a better mechanical strength and thus a better cell durability.

Fig. 5 shows the XRD patterns NiO-BZY/BZYZn bilayer (or half cell) of 20 μm thickness after co-sintering at 1450 °C. BZYZn electrolyte showed peaks characteristic of the parent BZY perovskite (JPCS card 74-1299), while the NiO-BZY anode shows characteristics peaks of BZY perovskite phase together with those of cubic NiO (JPCS card 47-1049). However both anode and electrolytes layers showed other very weak peaks attributed to BaY₂NiO₅ impurities (JPCS card 041-0463). The presence of such impurities has been already reported in literature and revealed a limited solid state reaction between the NiO and BZY perovskite containing a content Y mol% >0.1% at 1450 °C [35].

Cell test measurements and electrochemical characterization of single cells were performed in the temperature range 600–700 °C using 3% H₂O humidified hydrogen as fuel and static air at the cathode side. Fig. 6 shows the I–V and power density curves of cell 1 (4 h grounded anode) at different temperatures. The OCV values at different temperatures were slightly lower to the theoretical values and decreased with increasing temperature up to 700 °C. A

maximum power densities of 47, 69 and 90 mW cm^{−2} were achieved at 600, 650 and 700 °C, respectively.

Fig. 7 shows the impedance spectra of the cell 1 measured under open-circuit condition. The total resistance can be divided into ohmic resistance (R_{ohm}) and polarization resistance (R_p). Both R_{ohm} and R_p resistances increased with the decreasing of temperature from 1.01 to 1.28 Ω cm^{−2} and from 0.61 to 3.24 Ω cm^{−2}, respectively. However, R_p was predominant on the cell resistance, especially reducing the operating temperature.

In order to investigate the effect of the milling time of the anodic substrate, the electrochemical performance of cell 1 was compared with that of cell 2 (8 h grounded anode). Fig. 8 shows the relative I–V and power density curves of cell 1 and cell 2 compared with a previously developed Ni-BZY/BZYZn/Pt fuel cell with 100 μm thick BZYZn deposited by co-pressing [34] at 600 °C. The lowest tested temperature was chosen because it is the most suitable for intermediate temperature application and for comparison with comparable proton conductors cells from literature [5]. The open-circuit voltage (OCV) measured values of cell 1 and cell 2 were 0.93 and 0.94 V, respectively, slightly lower but still close to (above the 85%) the theoretical value, confirming the high density of the electrolyte in agreement with SEM analysis (Fig. 4). The OCV of thicker and co-pressed cell was 0.99 V, 90% of the theoretical value. The larger OCV value measured for the co-pressed electrolyte (100 μm) may be ascribed to the higher thickness in comparison to spun electrolyte layers (20 μm). The peak power densities at 600 °C were: 47, 75 and 17 mW cm^{−2} for cell 1, cell 2 and co-pressed cell, respectively. The power output of cell 2 with 20 μm thick BZYZn electrolyte spin coated on optimized anode is definitively the largest. At low current densities, the polarization curves of cell 1 and 2 show a smooth change of the slope (activation polarization region) which is mostly due to the slow oxygen reduction at the Pt electrode at 600 °C [6]. The same behavior cannot be observed in the co-pressed cell because of the poor performance.

Fig. 9 shows the impedance spectra of the same single cells measured under open-circuit condition. The ohmic resistance

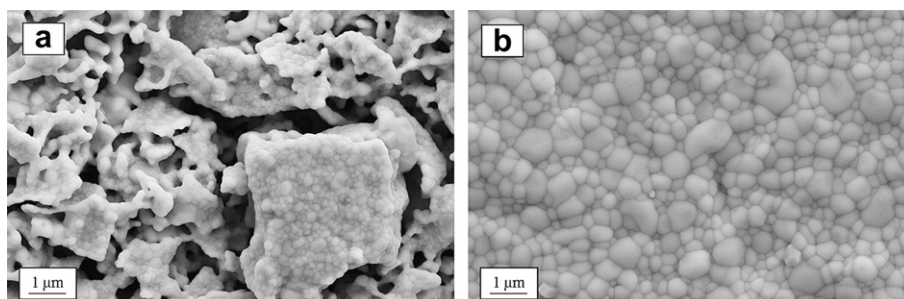


Fig. 3. SEM micrographs of the BZYZn electrolyte surface deposited onto a NiO-BZY anode using slurries obtained with 1 h (a) and 10 h milling time (b) After co-sintering at 1450 °C.

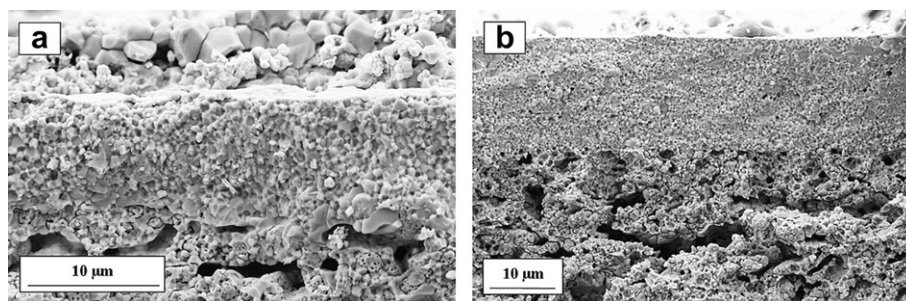


Fig. 4. SEM micrograph (cross section view) of a complete Ni-BZY/BZYZn/Pt cell with electrolyte thickness: (a) 10 μm and (b) 20 μm .

values of cell 2 ($1.15 \Omega \text{ cm}^{-2}$) is only slightly lower than R_{ohm} of cell 1 ($1.28 \Omega \text{ cm}^{-2}$) as reasonably expected given that the electrolytes of the two cell were fabricated in the same way (six spun layers). R_{ohm} of co-pressed cell is larger because of its higher thickness (100 μm). R_p of cell 2 ($2.60 \Omega \text{ cm}^{-2}$) is lower than both R_p of cell 1 ($3.24 \Omega \text{ cm}^{-2}$) and R_p of the co-pressed cell ($5.50 \Omega \text{ cm}^{-2}$), indicating that the use more uniform and better dispersed anodic cermet gives lower polarization resistance and thus better cell performance. In all investigated cells, R_p is predominant on the overall cell resistance, most probably because of the reduced cathodic performance of Pt on BZYZn at 600 $^{\circ}\text{C}$ [10]. Though it is clear that a suitable cathode for BZY-based fuel cells should be developed to improve cell performance, the data obtained allow to assess the efficiency of the processing protocol developed for the anodic half/cell. By spin coating it was thus possible to reduce and easily modulate the BZYZn film thickness and to produce

reproducible and performing anode supported button cells at the lab-scale.

While the processing of BZYZn has been widely investigated [21–24], only few electrochemical data regarding BZYZn based fuel cells have been reported in the literature [24,34]. A comparison of our results with the electrochemical performance of similar BZY-based fuel cells sintered with ZnO and other sintering aids is reported in Table 1. The cathode supported LSM + BZY-ZnO/BZY15-ZnO/Pt fuel cell with an electrolyte thickness of 30 μm deposited by

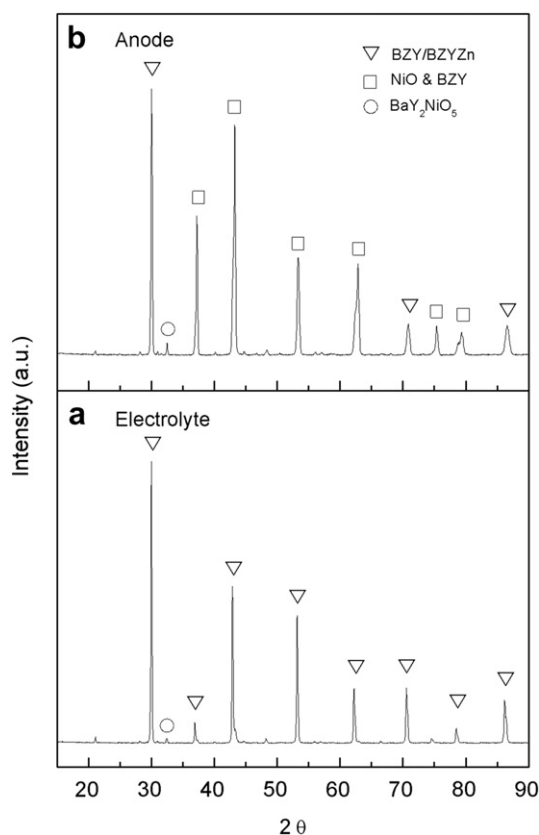


Fig. 5. XRD patterns of the half cell (anode and electrolytes) after co-sintering at 1450 $^{\circ}\text{C}$: electrolyte layer (a) and anode substrate (b).

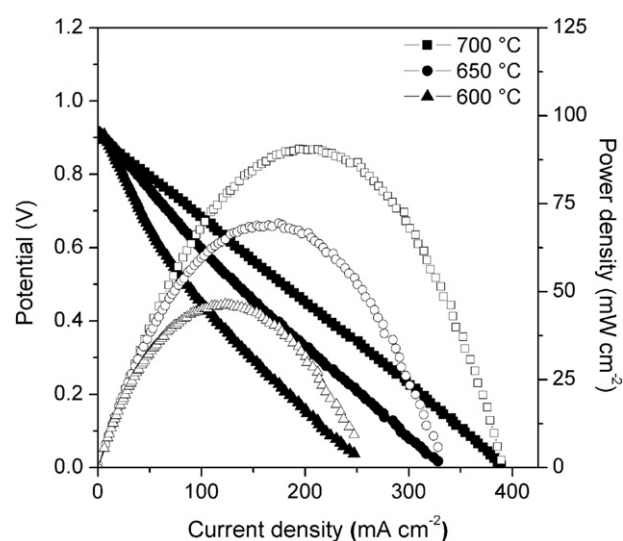


Fig. 6. I–V (closed symbol) and power density (open symbol) curves of cell 1 at different temperatures in wet H_2 ($\sim \text{H}_2\text{O}$).

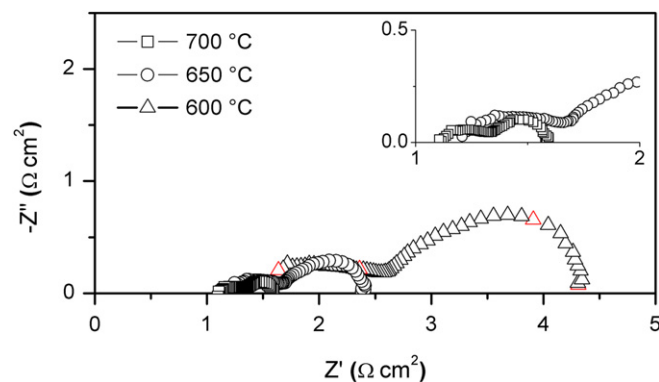


Fig. 7. Nyquist plots under open circuit condition of cell 1 at different temperatures in wet H_2 ($\sim \text{H}_2\text{O}$). In the inset, an enlargement at high frequency.

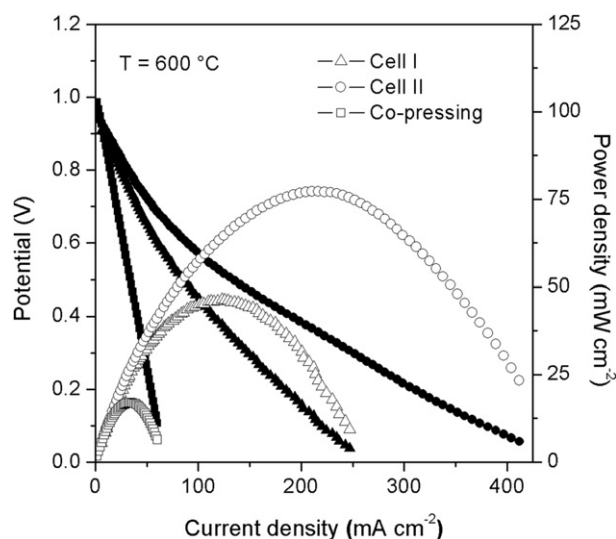


Fig. 8. I–V (closed symbol) and power density (open symbol) curves of cell 1 at 600 °C in wet H₂ (~H₂O).

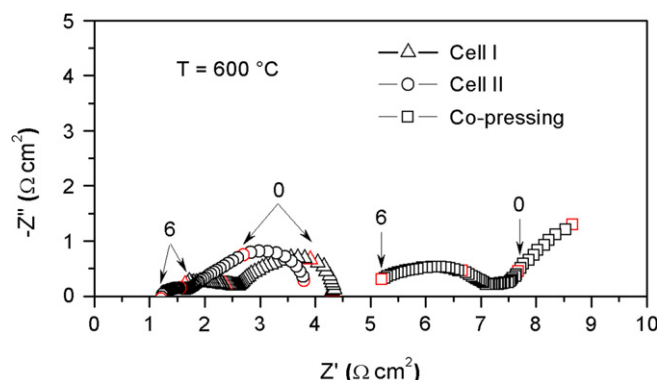


Fig. 9. Nyquist plots under open circuit condition of Ni-BZY/BZYZn/Pt cells at 600 °C in wet H₂ (~H₂O). Numerical labels indicate log₁₀ of applied frequency.

using spin-coating deposition and co-firing process reported in [24] shows a much lower power density output, 25 mW cm⁻² at 800 °C. The maximum power density of Ni-BZY/BZYZn/Pt single cell with a 100 μm thick electrolyte deposited by co-pressing was achieved at 700 °C and is equal to 27 mW cm⁻² [34], well below our results obtained at 600 °C.

The peak power density of cells with BZY doped with LiNO₃ electrolyte obtained by co-pressing is 53 mW cm⁻² at 700 °C [19], while the performance of CuO doped BZY based cell in an

electrolyte supported configuration is 2.6 mW cm⁻² at 800 °C [20], both definitely lower than that of the present work.

Finally, comparing our results with those of anode supported BZY-based cell (without ZnO sintering aid) with configuration: BZY + NiO/BZY20/BSCF (Ba_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}) obtained by co-pressing and using a sintering temperature of 1450 °C (electrolyte thickness 30 μm), it can be noted that the power density output was 45 mW cm⁻² at 700 °C [12] still lower than our results at 600 °C thus, it can be concluded that ZnO doping is effective not only in improving the sinterability of BZY, but also in enhancing the power density output improving the overall cell performance.

4. Conclusions

A spin-coating method was developed to fabricate BZY based electrolytes fuel cells by using ZnO as a sintering aid. The electrolyte thickness can be easily controlled by changing the number of spun layers while a co-sintering temperature as low as 1450 °C was used to densify the electrolyte. Electrochemical measurements showed promising performances, higher than data reported in the literature on comparable cells. Work is in progress to improve the cell performances by developing a proper cathodic material.

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Table 1

Performance of BZY-based fuel cells with different sintering aids.

Electrolyte	Fuel cell	Deposition	PPD (mW cm ⁻²)	Ref.
BZY15_ZnO	LSM + BZY-ZnO/ BZY15_ZnO/Pt	Spin-coating 30 μm	25 at 800 °C	[24]
BZY20_ZnO	Ni + BZY/BZY20_ ZnO/Pt	Co-pressing 100 μm	27 at 700 °C	[34]
BZY20_Li	BZY20 + NiO/ BZY20_Li/BZY20 + LSCF	Co-pressing 25 μm	53 at 700 °C	[19]
BZY10_CuO	Pt/BZY10_CuO/Pt	Electrolyte- supported 1.2 mm	2.6 at 800 °C	[20]
BZY20_ZnO	BZY20 + NiO/ BZY20_Zn/Pt	Spin-coating 20 μm	75 at 600 °C	Present work

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